

# Polymer adhesion: first-principles calculations of the adsorption of organic molecules onto Si surfaces.

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The structures and energetics of organic molecules adsorbed onto clean and H-passivated Si(001)-(2×1) surfaces have been calculated using density functional theory. For benzene adsorbed on the clean Si surface the tight-bridge structure was found to be stable and the butterfly structure metastable. Both carbonic acid  $\text{H}_2\text{CO}_3$  and propane  $\text{C}_3\text{H}_8$  dissociate on contact with the surface. Passivation of the Si surface with H-atoms has a dramatic effect on the surface properties. The passivated surface is very inert and the binding energy of all the molecules is very weak.

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The adsorption of organic molecules on semi-conductor surfaces is of increasing importance to industry due to interest in the development of organic optoelectronic devices, micro/molecular-scale electronics and biofunctionality [1, 2, 3]. An additional motivation for studying these systems is to understand the nature of adhesion between plastics and metal or ceramic surfaces. Many of these materials do not adhere well and the main focus of this research is to obtain a better understanding of the structure and bonding at the polymer-surface interface.

While oxide/ceramic surfaces are primarily of interest, we have chosen to first study the simpler Si(001) surface, which is easier to simulate and will provide the initial insight into the nature of the bonding at surfaces. This will provide the basis for future work involving the more complex silica surface. The plastic of interest is mainly composed of the polymer bisphenol-A-polycarbonate (BPA-PC). The repeat unit, or monomer, is shown in Figure 1. This polymer has been extensively studied with

molecule on a surface. It is, therefore, necessary to divide the monomer into its analogous molecules (benzene, propane and carbonic acid as shown in Figure 1) and study their individual adsorption on the surface. The results of these first-principles calculations could then be used to build potentials for coarse-grained simulations, so these calculations are the first step towards a multiscale study.

For low density systems, such as molecular adsorption, van der Waals forces can play a significant role. Recently a method for including the van der Waals energy within density functional theory (DFT) was suggested [8, 9] and has been shown to determine the correct binding distances and energies for benzene dimers [10, 11] and for benzene and naphthalene adsorbed on graphite [12, 13]. However, it is known that benzene binds strongly to Si and the additional binding due to van der Waals forces will be small compared to the chemical binding energies. Thus, the effect of van der Waals forces has not been taken into account in this paper.

The paper is organised as follows: Section I describes the two Si surfaces under consideration and gives the technical details of the calculations. Sections II and III describe the adsorption of benzene and the other organic molecules on the clean and H-passivated Si dimer surfaces, denoted Si(001)-(2×1) and Si(001):H-(2×1), respectively. The discussion and conclusions appear in Section IV.

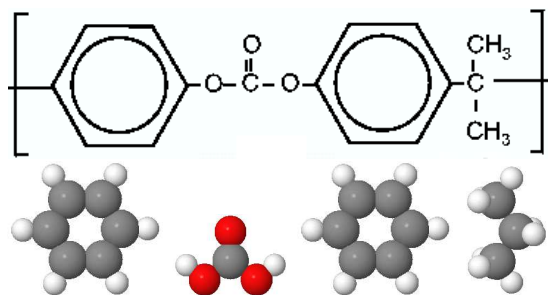


FIG. 1: (Color online) The monomer bisphenol-A-polycarbonate (BPA-PC) and its analogous molecules benzene ( $\text{C}_6\text{H}_6$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), another benzene and propane ( $\text{C}_3\text{H}_8$ ).

both first-principles methods [4, 5, 6] and coarse-grained molecular dynamics simulations [7].

To understand the nature of adhesion it is necessary to consider processes which occur at different time, length and temperature scales and therefore a multiscale study is desirable. First-principles calculations provide details in the microscopic regime but they are too computationally demanding to be able to treat the entire polymer

## I. SI(001)-(2×1) AND SI(001):H-(2×1) SURFACES

At room temperature the Si(001) surface has a (2×1) structure, which consists of the formation of buckled dimers, with one atom being drawn towards the surface closer to its three nearest neighbours, and the other being pushed away from its neighbours, as shown in Figure 2. As the clean Si(001)-(2×1) surface is rather reactive, adsorbed atoms or molecules, such as H or  $\text{H}_2\text{O}$ , are likely to be present and, therefore, we have also considered adsorption on the H-passivated Si(001):H-(2×1) surface. The H-(2×1) surface is passivated by one H atom

per Si atom, as shown in Fig. 2.

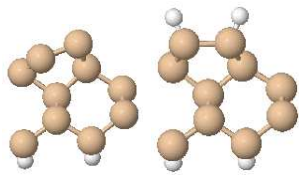


FIG. 2: (Color online) The clean Si(001)-(2 $\times$ 1) dimer reconstruction (left) and H-passivated Si(001):H-(2 $\times$ 1) surface (right) viewed along the [110] direction.

First-principles calculations were performed with the Vienna *Ab initio* Simulation Package (VASP) [14, 15], which implements density functional theory. The PW91 flavour [16, 17] of the generalised-gradient approximation (GGA) and projector augmented-wave potentials (PAW) [18] were used. The plane-wave energy cutoff was 400 eV, which corresponds to an error in the total energy of  $\approx 3$  meV per Si atom, and the Brillouin zone mesh was equivalent to a  $4 \times 4 \times 1$  Monkhorst-Pack  $k$ -point sampling for a 0.5 ML supercell with dimensions (1 1 0) (-1 1 0) (0 0 4). The calculated lattice constant of bulk Si is 5.47 Å.

For the slab calculations we used a 5-atomic layer Si slab and  $\approx 15$  Å of vacuum. All relaxations were considered complete when the forces were less than  $10 \text{ meV Å}^{-1}$ . To save computational time only adsorption on one side of the slab was considered. When the slab is asymmetric and periodic boundary conditions are used, as is the case in these calculations, it must be ensured that there is no dipole-dipole interaction between the slabs. The energy of the dipole-dipole interaction is inversely proportional to the distance between the slabs so one way to avoid this interaction is to have a large vacuum region between slabs. To check this the vacuum was increased from  $\approx 15$  Å to  $\approx 25$  Å and it was found that the adsorption energies did not change. This indicates that the dipole-dipole interaction is negligible. For both the clean and H-passivated slabs the bottom layer of the slab was fixed in the bulk Si positions and passivated with two H atoms per Si atom. The Si(001)-(2 $\times$ 1) surface structure of a 9-atomic layer slab was also calculated and the differences between the 9 and 5-atomic layer slabs were small, i.e. the dimer bond lengths are 2.31 Å and 2.30 Å and the angles are  $18.11^\circ$  and  $18.02^\circ$ , respectively. Increasing the plane-wave cut-off energy to 600 eV does not change these values. To check that the chemisorption energies are converged we also calculated the benzene adsorption energies on an 9-atomic layer slab (see subsection II A). The results presented in the paper use H-passivated 5-atomic layer slabs and a cut-off of 400 eV unless otherwise indicated. For the Si(001):H-(2 $\times$ 1) surface the H-passivation caused the dimer to flatten and the bondlength to increase to 2.42 Å, in agreement with Zanella *et al* [19].

## II. ADSORPTION ON SI(001)-(2 $\times$ 1)

### A. Benzene, C<sub>6</sub>H<sub>6</sub>

There are several publications which report the structural geometry and energetics of benzene adsorbed on Si(001)-(2 $\times$ 1). Five different geometries have been studied in the literature: two single dimer di- $\sigma$  bonded structures named “tilted” and “butterfly”, and three double dimer tetra- $\sigma$  bonded structures: “tight bridge”, “twisted bridge” and the symmetric bridge (“pedestal”). The two most stable structures are agreed to be the butterfly and tight-bridge structures but to date there is no conclusive experimental or computational study that determines which structure is the stable one and which is metastable. Here we make a comprehensive overview of the available data and present results for benzene adsorption at low coverages.

#### 1. Structural data

Figures 3 and 4 show the butterfly and tight-bridge structures, respectively. The butterfly structure is bonded to the two dangling bonds of a single Si-Si dimer whereas the tight-bridge structure is bonded to two Si-Si dimers. These adsorption structures are significantly distorted compared to the isolated benzene molecule. Another distinguishing feature is that the butterfly structure has a symmetry plane along the Si-dimer.

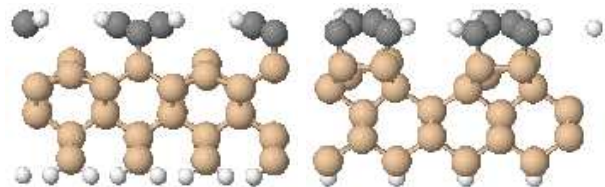


FIG. 3: (Color online) “Butterfly” structure of C<sub>6</sub>H<sub>6</sub> on Si(001)-(2 $\times$ 1) viewed along  $\bar{1}10$  and  $[110]$  (dimer rows), respectively.

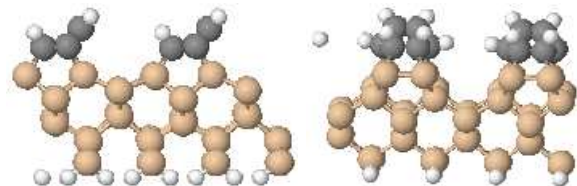


FIG. 4: (Color online) “Tight-bridge” structure of C<sub>6</sub>H<sub>6</sub> on Si(001)-(2 $\times$ 1) viewed along  $\bar{1}10$  and  $[110]$ , respectively.

Our structural data for both geometries is in excellent agreement with previous first-principles results (see Tables I and II). In the butterfly structure the benzene

adopts a V-shape as shown in Fig 3. The Si dimer bond length is 2.39Å, which is in excellent agreement with Hofer *et al* [20].

Si-Si	Si <sub>C</sub> -Si <sub>C</sub>	Si <sub>C</sub> -C <sub>Si</sub>	C-C <sub>Si</sub>	C=C	Reference
2.34	2.39	1.98	1.50	1.35	Present
2.24	2.34	-	1.51	1.34	[21]
-	2.39	1.98	1.50	1.34	[20]
-	-	1.89	1.47-1.49	1.35	[22]
-	2.46	1.97	1.51	-	[23]

TABLE I: Bond lengths (Å) for the butterfly geometry. Si<sub>C</sub> and C<sub>Si</sub> denote Si atoms bonded to C and C atoms bonded to Si, respectively.

Si <sub>C</sub> -Si <sub>C</sub>	Si <sub>C</sub> -C <sub>Si</sub>	C <sub>Si</sub> -C <sub>Si</sub>	C-C <sub>Si</sub>	C=C	Reference
2.35-2.38	1.99-2.00	1.57-1.58	1.50	1.35	Present
2.34	1.98-2.00	1.58-1.59	1.51	1.34	[21]
2.39	1.98-2.01	1.57	1.50	1.35	[20]
-	1.87-1.89	1.47-1.53	-	1.35	[22]

TABLE II: Bond lengths (Å) for tight-bridge geometry.

## 2. Stability – experimental evidence

According to a scanning tunnelling microscopy (STM) study by Lopinski *et al* [24], the benzene molecule adsorbs initially in the butterfly structure but this is observed to be metastable with respect to a bridging configuration. They were able to convert the benzene from one structure to another using the STM tip and estimated the conversion barrier to be 0.95 eV.

Gokhale *et al* [25] used thermal desorption spectroscopy (TPD) and angle-resolved photoelectron spectroscopy (ARUPS) to investigate the electronic structure and symmetry of benzene on Si and observed a single dimer structure, supporting the butterfly configuration.

Witkowski *et al* [26] used near-edge x-ray-absorption fine-structure (NEXAFS) to look at the structure of the adsorbed benzene and found the benzene to be symmetric with respect to the dimer axis, ruling out the tight-bridge structure. These findings were supported by reflectance anisotropy spectroscopy (RAS) and surface differential reflectivity spectroscopy (SDRS) data [27], which found that benzene adsorbs on top of a single dimer rather than on the bridge site between two dimers.

The high-resolution photoemission study by Kim *et al* [28] suggested that the adsorption geometry depends on the coverage[37]. They found that at low coverages a bridging structure is favoured but that at high coverages a single dimer structure is more stable. This result is consistent with the previous experiments as the STM measurements were carried out at a low coverage and the TPD, ARUPS, NEXAFS, RAS and SRDS ex-

periments were carried out at the saturation coverage of 0.5 ML[25, 27, 28].

## 3. Adsorption energies

DFT studies of benzene adsorbed on silicon all agree that the tight-bridge structure is stable with the butterfly structure being metastable[20, 29, 30]. Lee *et al* [29] studied the tight-bridge and butterfly states using VASP and US/norm-conserving (NC) pseudopotentials. For a coverage of 0.5 ML the tight-bridge structure was more stable with an adsorption energy of 1.05 eV. The adsorption energy of the butterfly structure was 0.82 eV. They also studied the conversion between the butterfly and tight-bridge states and found an high energy barrier of 0.87 eV, which means that both states could coexist. This supports the STM findings [24] but disagrees with other experiments. A comparison between the present adsorption energies and those of previous studies is shown in Table III.

Adsorption energy (eV molecule <sup>-1</sup> )		Details <sup>a</sup>	Reference
TB	BF		
1.21	0.99	9, 400 eV, US	Present
1.26	1.01	9, 600 eV, PAW	Present
1.25	1.00	9, 400 eV, PAW	Present
1.21	1.02	5, 400 eV, PAW	Present
0.98	0.88	6, 350 eV, US	[30]
1.05	0.82	5, 340 eV, US/NC	[29]
1.18	-	8, 300 eV, US	[20]

<sup>a</sup>The details are as follows: atomic layers of Si in slab, plane-wave cut-off energy, pseudopotential type. All the calculations used either the PW91 or PBE GGAs, which are similar.

TABLE III: Adsorption energies of benzene in the tight-bridge (TB) and butterfly (BF) geometries for a coverage of 0.5 ML.

In the calculations shown in Table III the adsorption energies cover a rather large range, which could be due to different pseudopotentials or supercell size. All the results used the PW91 or PBE[31, 32, 33] GGA's, which should give similar results. The current calculations are the most accurate calculations to date and we have tested the effect of using different slab thicknesses and pseudopotentials. Although these make some small changes to the adsorption energies they do not explain the large variation seen in the literature and hence we must attribute the differences to other convergence parameters.

## 4. Coverage dependence

Molecular coverage can also have a significant effect on adsorption as demonstrated by Kim *et al* [28], who observed that the structure of the adsorbed benzene is coverage dependent, with the butterfly structure stable

at high coverages. Results for a range of coverages are presented in Tables IV and V. For the 0.25 ML coverages two supercell orientations are possible. Supercells (a) and (b) have primitive lattice vectors (220) ( $\bar{1}10$ ) (006) and (110) ( $\bar{2}20$ ) (006), respectively, with the dimer rows along the  $\bar{1}10$  direction. Supercell (b) has four dimers along the dimer row.

Coverage (ML)	Adsorption energy (eV)				
	Present	Lee [29]	Hofer [20]	Jung [21]	
	5-layer	9-layer			
Isolated	-	-	-	-	0.96
0.125	1.25	1.34	-	-	-
0.25 (a)	1.23	1.27	-	-	-
(b)	1.24	1.35	0.91	1.42 <sup>a</sup>	-
0.5	1.21	1.25	1.05	1.18	-

<sup>a</sup>Supercell not specified

TABLE IV: Variation of adsorption energy with coverage for the tight-bridge structure.

Coverage (ML)	Adsorption energy (eV)				
	Present	Lee [29]	Hofer [20]	Jung [21]	
	5-layer	9-layer			
Isolated	-	-	-	-	1.04
0.125	1.07	1.06	-	-	-
0.25 (a)	1.04	1.03	-	-	-
(b)	1.05	1.04	0.84	1.12 <sup>a</sup>	-
0.5	1.02	1.00	0.82	-	-

<sup>a</sup>Supercell not specified

TABLE V: Variation of adsorption energy with coverage for the butterfly structure.

The butterfly structure was found to be unstable at a coverage of 1 ML, which is consistent with the experimental saturation coverage of around 0.5 ML [25, 27, 28]. To obtain a 1 ML coverage for the tight-bridge structure the Si dimers would have to be shared between the benzene molecules and, thus, for this case a coverage of 1 ML is unrealistic.

The present results show a small variation in adsorption energies for coverages of 0.125-0.5 ML and for all coverages the tight-bridge structure remains stable. The adsorption energies for the butterfly structure do not change significantly when the slab is increased from 5 to 9 layers. However for the tight-bridge structure additional relaxation in the 9-layer slab results in higher adsorption energies, particularly for the 0.25(b) and 0.125 ML coverages.

Hofer *et al* [20] found that increasing the coverage from 0.25 ML to 0.5 ML decreased the binding energy of the tight-bridge structure by 0.24 eV, which was attributed to a relaxation of the strain within the cell. This agrees qualitatively with the present results, which show a smaller decrease in the tight-bridge adsorption energy of 0.1 eV. These results disagree with the DFT results of Lee *et al* [29], who observed an increase of 0.14 eV.

There are two possible scenarios which could explain the conflicting experimental and theoretical evidence. The first possibility is that the benzene molecule adsorbs initially in the butterfly structure [24] (there is no barrier for this reaction as shown in Figure 11) but this is metastable with respect to a bridging configuration. The conversion barrier was estimated to be 0.95 eV, which is in good agreement with the DFT calculations of Lee *et al* [29], who found the conversion barrier to be 0.87 eV. The barrier is high enough to allow the butterfly configuration to exist for a relatively long time, which could explain why other experimental methods have observed the butterfly structure.

The second possibility is that the inclusion of van der Waals forces will affect the stabilities. One of the drawbacks of density functional theory is that it does not include van der Waals forces, which are due to dynamical correlation. Even though benzene binds strongly to Si and the additional binding due to van der Waals forces will be small compared to the chemical binding energies, the van der Waals forces may be large enough to overcome the energy differences between the two structures and stabilise the butterfly structure. The quantum mechanics/molecular mechanics (QM/MM) method used by Jung *et al* [21] included van der Waals forces by using single-point energy calculations with multireference second-order perturbation theory (MRMP2). They found that for an isolated molecule on a Si cluster the butterfly structure was more stable than the tight-bridge structure, with adsorption energies of 1.04 and 0.96 eV, respectively. However, they used a small Si cluster, which may not be large enough to represent the Si surface accurately, so it is not clear whether this result is valid. Furthermore, the cluster geometry corresponds to an isolated molecule i.e. a low coverage system, which according to Kim *et al* is in the regime where the tight-bridge structure should be stable.

## B. Carbonic acid, H<sub>2</sub>CO<sub>3</sub>

When carbonic acid is placed on the clean Si surface it dissociates with one O and two H atoms bonding to the Si surface and a CO<sub>2</sub> molecule being left over. The energy vs. distance of the H<sub>2</sub>CO<sub>3</sub> approaching the surface was obtained by fixing the distance of the C atom from the surface and relaxing the molecule and surface. This shows that there is no energy barrier to overcome to enable this reaction to occur.

To avoid the problem of dissociation it is necessary to consider the possible conformations of carbonic acid within the BPA-PC chain. The structure of this section of BPA-PC is shown in Figure 5.

Based on our knowledge of benzene adsorption on Si the most stable structure is likely to have the two phenol rings adsorbed in the tight-bridge structure, as shown in Figure 6. The molecule is arranged so that the CO<sub>3</sub> group is attached to the top of the two tight-bridge struc-



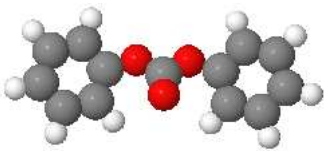


FIG. 5: (Color online) The  $\text{C}_6\text{H}_5\text{CO}_3\text{C}_6\text{H}_5$  molecule represents part of the BPA-PC monomer containing the carbonate group.

tures. Several orientations of the  $\text{CO}_3$  group within the adsorbed  $\text{C}_6\text{H}_5\text{CO}_3\text{C}_6\text{H}_5$  molecule were calculated and the orientation with the minimum energy has the C–O double bond pointing upwards and inwards, as shown in Figure 6. The adsorption energy of the whole molecule

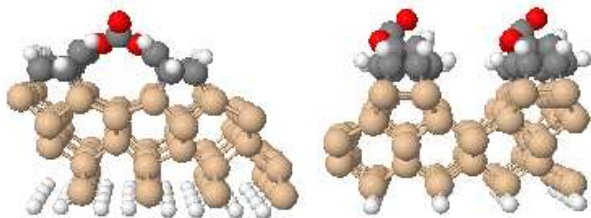


FIG. 6: (Color online) The lowest energy adsorption structure of  $\text{C}_6\text{H}_5\text{CO}_3\text{C}_6\text{H}_5$  adsorbed on Si. Both phenol rings have the tight-bridge structure. LHS: viewed along  $[\bar{1}10]$ . RHS: viewed along  $[110]$  dimer rows.

is 1.83 eV. By subtracting the adsorption energy of the two tight-bridge structures from this adsorption energy we estimated the adsorption energy of the  $\text{CO}_3$ -group to be -0.59 eV. This means that the  $\text{CO}_3$  experiences a repulsive force from the Si surface.

Other adsorption configurations for this molecule are unlikely as the  $\text{CO}_3$  cannot stretch from a tight-bridge to a butterfly configuration or from the high point of one tight-bridge to the low point of an adjacent tight-bridge. However, the adsorption barrier for this structure may be high since due to the geometrical constraints it may be difficult for both benzenes to initially adsorb in the butterfly structure.

### C. Propane, $\text{C}_3\text{H}_8$

Similar to the case of carbonic acid, the propane molecule dissociates on the surface, with the two H atoms bonding to the surface. As before, we need to consider a larger segment of BPA-PC which contains the propane group.

The isolated molecule is shown in Figure 7 and the molecule adsorbed on the Si surface is shown in Figure 8. Geometrically the propane group cannot bond to two tight-bridge structures but it may bond to a tight-bridge on one side and the butterfly geometry on the other. The



FIG. 7: (Color online) The isolated  $\text{C}_6\text{H}_5\text{C}_3\text{H}_6\text{C}_6\text{H}_5$  molecule which is a segment of BPA-PC containing the propane group.

lowest energy structure for this configuration is shown in Figure 8 and the adsorption energy of the whole molecule is 1.59 eV. The estimated adsorption energy of the  $\text{C}_3\text{H}_6$ -group is -0.64 eV, which corresponds to a repulsive force from the surface.

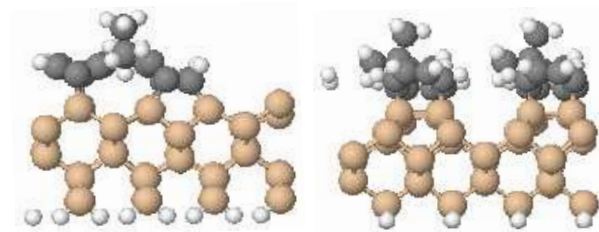


FIG. 8: (Color online)  $\text{C}_6\text{H}_5\text{C}_3\text{H}_6\text{C}_6\text{H}_5$  on  $\text{Si}(001)-(2\times 1)$  viewed along  $[\bar{1}10]$  and  $[110]$ , respectively.

## III. ADSORPTION ON $\text{Si}(001):\text{H}-(2\times 1)$

The clean Si surface is very reactive so it is interesting to know how this compares to the H-passivated surface. Six adsorption sites have been considered and are shown in Figure 9. Sites A,B,C and D are high symmetry positions, site F is above a surface H atom and site E is the midpoint between two surface H atoms.

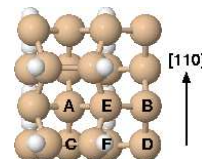


FIG. 9: (Color online) Adsorption sites on  $\text{Si}(001):\text{H}-(2\times 1)$ .

### A. Benzene, $\text{C}_6\text{H}_6$

There are two orientations for the benzene molecule, denoted I and II. Orientation I has two of the C–C bonds in the benzene ring perpendicular to the Si–Si dimers and orientation II is obtained by rotating I by  $30^\circ$  around the

vertical axis. As an example, benzene placed on site C with orientation II, is shown in Figure 10.

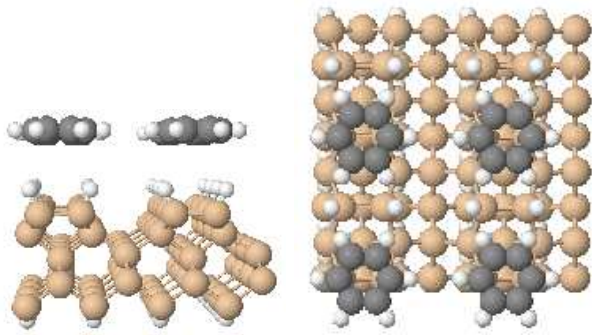


FIG. 10: (Color online) Side and top views of benzene adsorbed on site C of the Si(001):H-(2 $\times$ 1) surface and with orientation II.

For all sites and orientations the adsorption of benzene is very weak, with adsorption energies of 0.06-0.07 eV and equilibrium distances between the benzene and the surface H-atoms of 3.2-3.4 Å. The benzene molecule remains flat in contrast to the large distortion seen in the case on the clean Si surface.

The difference between the adsorption behaviour of benzene on the clean Si surface and its behaviour on the passivated surface is further demonstrated by looking at the variation of the adsorption energy as a function of distance from the surface, which is shown in Figure 11. On the clean Si surface it is known that benzene initially adsorbs in the butterfly configuration, so for convenience the benzene was placed in configuration CII on each surface. For a particular separation distance the position of one of the C-atoms was fixed and the rest of the benzene molecule and the surface were allowed to relax. For the clean surface it was convenient to fix either of the C atoms above the dimer Si atoms and the distance was defined as the difference between the z-position of the fixed carbon atom and the average z-position of the two Si dimer atoms in the minimum energy configuration. For the passivated surface the distance was defined as the distance from the fixed carbon atom to the z-position of the surface H-atoms at the minimum energy configuration. The position of the H atoms is not significantly different for the various benzene configurations. As can be seen from Figure 11 there is no barrier for adsorption into the butterfly configuration on the clean Si surface. For the H-passivated surface, the benzene experiences significant repulsion as it approaches the surface and thus the benzene sees the surface as a approximately uniform hard wall.

The binding energies for the passivated surface are small and therefore to get the true adsorption energies and equilibrium distances of these molecules it is necessary to consider van der Waals interactions. Based on calculations of phenol on alumina [12] and phenol on graphite [13] we estimate the van der Waals energy to

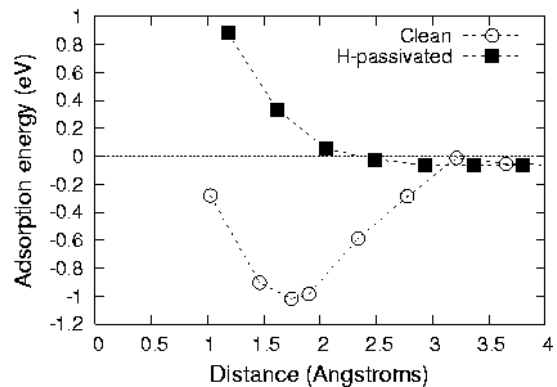


FIG. 11: Barriers for adsorption of C<sub>6</sub>H<sub>6</sub> on site CII of Si(001)-(2 $\times$ 1) and Si(001):H-(2 $\times$ 1).

be of the order of 0.2-0.5 eV.

### B. Carbonic acid, H<sub>2</sub>CO<sub>3</sub>

There are four possible orientations for the H<sub>2</sub>CO<sub>3</sub> molecule to adsorb on the H-passivated Si(001) surface. These are I) parallel to a dimer with the double-bonded O on top, II) perpendicular to a dimer with the double-bonded O on top, and III) parallel with the double-bonded O pointing down and IV) perpendicular with the double-bonded O pointing down. Configuration BIII is shown in Figure 12.

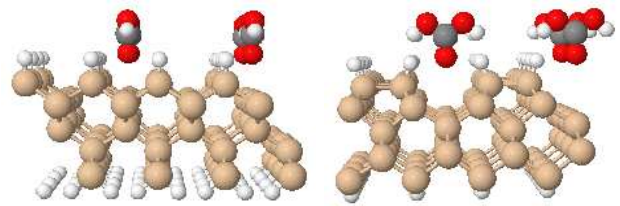


FIG. 12: (Color online) Carbonic acid molecule adsorbed on the H-passivated Si surface with configuration BIII. LHS: viewed along  $[110]$ . RHS: viewed along  $[1\bar{1}0]$  dimer rows.

The binding energies for all the sites range from 0.04-0.10 eV and the distance of the carbon atom in H<sub>2</sub>CO<sub>3</sub> from the surface hydrogen atoms ranges from 1.6-4.2 Å. The maximum binding energy and minimum adsorption distance occurs for configuration BIII and as can be seen from Figure 12 this is mainly due to topology.

### C. Propane, C<sub>3</sub>H<sub>8</sub>

There are four possible orientations in which propane could adsorb. In I and III the carbon chain is parallel to the dimers, whereas in II and IV the carbon chain is perpendicular to the dimers. For I and II the carbon-chain

makes a “V-shape” on the surface and III and IV the carbon-chain is inverted to make an upside down “V”. Figure 13 shows the propane molecule in site C and orientation I, in which the “V-shape” can be seen on the right. Similar to benzene and carbonic acid, propane is

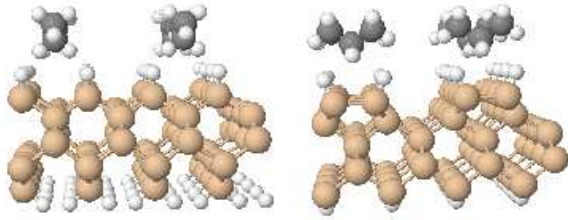


FIG. 13: (Color online) Propane molecule adsorbed on the H-passivated Si surface with configuration CI. LHS: viewed along  $[110]$ . RHS: viewed along  $[110]$  dimer rows.

also very weakly bound to the surface with adsorption energies ranging from 0.04-0.06 eV. For orientations I and II the vertical distance from the central C in propane to the surface H-atoms is 2.5-3.4 Å and for orientations III and IV it is 3.8-4.2 Å.

#### IV. SUMMARY AND DISCUSSION

The adsorption behaviour of benzene, carbonic acid and propane on the Si(001)-(2×1) and Si(001):H-(2×1) surfaces was calculated. For the Si(001)-(2×1) surface the stable adsorption structure of benzene was found to be the tight-bridge structure with an adsorption energy of 1.26 eV. The butterfly structure is metastable with an adsorption energy of 1.01 eV. The carbonic acid and propane molecules were found to spontaneously dissociate on the surface.

To avoid the issue of dissociation, the adsorption behaviour of larger segments of the BPA-PC chain was studied. These segments correspond to carbonic acid bonded to two benzene rings and propane bonded to two benzene rings. Trial structures of these large molecules were calculated and the results were used to estimate adsorption energies of the  $\text{CO}_3$  and  $\text{C}_3\text{H}_6$  groups. It was found that these groups are repelled from the Si surface.

Combined DFT/coarse-grained studies of BPA-PC on Ni(111) have already been published [34, 35]. The first-principles calculations showed that benzene binds strongly to the Ni surface but that carbonic acid and propane experience significant repulsion. The behaviour of these molecules on Si is very different to their behaviour on Ni(111). The adsorption energy of benzene

on Ni is 1.05 eV [34], which is comparable to the adsorption energy of benzene on Si. The geometries, however, are very different, and on the Ni surface the benzene remains relatively undistorted at a centre-of-mass distance of 2 Å. In contrast, propane and carbonic acid see the Ni surface as a uniform hard wall and they experience significant repulsion for distances shorter than 3.2 Å. By incorporating this data into a coarse-grained model, they showed that the phenol chain ends bind to the Ni surface and that the rest of the polymer is repelled away from the surface.

An important point to note is that the trial adsorption structures for the BPA-PC segments, described above, may not be geometrically compatible with the larger BPA-PC chain. The polymer chain must be continued from the low point of the tight-bridge structure and if the repulsion of the  $\text{C}_3\text{H}_6$  group is strong enough this benzene may desorb from the surface. In this case the “internal” benzene groups may not approach the surface and only the benzene chain ends may adsorb. If this is the case, then despite the differences in molecular adsorption behaviour the behaviour of a BPA-PC chain on Si may turn out to be similar to that of BPA-PC on Ni.

Passivation of the Si surface with H-atoms has a dramatic effect on the surface properties. The passivated surface is very inert and the binding energy of all the molecules is extremely weak. Due to the weak binding of this system the van der Waals interaction becomes dominant and to get a true picture of the binding in this case it would be necessary to include the van der Waals energy.

Another physical effect that is missing in the DFT formalism is the image charge potential. This has been addressed in a recent study of adsorbed molecules on graphite [36]. The image charge affects, in particular, the excited-state energy levels but not the adsorption energies.

This work provides the first step in multiscale simulations of the adhesion of polymers to surfaces. The first-principles calculations presented in this paper can now be used to build potentials for coarse-grained simulations.

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